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Spacer engineering of diammonium-based 2D perovskites towards efficient and stable 2D/3D heterostructure perovskite solar cells

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Abstract

Perovskite solar cells (PSCs) based on 2D/3D heterostructures show great potential to combine the advantages of high efficiency of the 3D perovskites and high stability of the 2D perovskites. However, an in-depth understanding of the organic-spacer effects

1 on the 2D quantum well (QW) structures and electronic properties at the 2D/3D
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4 interfaces is yet to be fully achieved, especially in the case of 2D perovskites based on
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6 diammonium spacers/ligands. Here, a series of diammonium spacers was considered
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9 to construct 2D/3D perovskite heterostructures. It is found that the chemical structure
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11 and concentration of the spacers can dramatically affect the characteristics of the 2D
12
13 capping layers, including their phase purity and orientation. Density functional theory
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15 calculations indicate that the spacer modifications can induce shifts in the
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17 energy-level alignments at the 2D/3D interfaces and therefore influence the
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19 charge-transfer characteristics. The strong intermolecular interactions between the
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21 2,2-(ethylenedioxy)bis(ethylammonium (EDBE) cations and inorganic $[\text{PbI}_6]^{4-}$ slabs
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23 facilitate a controlled deposition of a phase-pure QW structure ($n=1$) with horizontal
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25 orientation, which leads to better surface passivation and carrier extraction at the
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27 2D/3D interfaces. These benefits endow the EDBE-based 2D/3D devices with a high
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29 power conversion efficiency (PCE) of 22.6% and remarkable environmental stability,
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31 highlighting the promise of spacer-chemistry design for high-performance 2D/3D
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33 PSCs.
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47 **Introduction**

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50 Currently, long-term stability is the major obstacle to the commercialization of
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52 metal halide perovskite solar cells (PSCs).^[1, 2] For PSCs based on three-dimensional
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54 (3D) bulk perovskites, although the phase stability can be improved by fine tuning the
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56 Goldschmidt tolerance factor through composition engineering, the environmental
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1 stability of the perovskite films is generally poor due to their susceptibility to
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3 moisture- and oxygen-induced chemical degradation.^[3-5] To overcome the intrinsic
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5 stability issues, bulky organic ligands can be introduced into 3D perovskites to form
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7 two-dimensional (2D) perovskites, where they appear as spacers between perovskite
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9 layers and provide a much improved structural stability.^[6, 7] The organic spacers in the
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11 2D perovskite have hydrophobic segments that can effectively prevent moisture
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13 permeation and also improve phase stability.^[8] The ion migration that easily occurs in
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15 3D perovskites can also be mitigated due to the bulkiness of the spacers in the 2D
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17 perovskites.^[9] However, reducing the crystal dimension from 3D to 2D also results in
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19 quantum and dielectric confinements, which contribute to higher optical gaps and
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21 exciton-binding energies in 2D perovskites.^[10] Moreover, the heterogeneity in crystal
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23 orientation and the insulating character of the spacer layers hinder the efficiency of
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25 charge transport between neighboring inorganic sheets.^[11] These issues therefore limit
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27 the device efficiency of 2D PSCs, which still lags significantly behind that of 3D
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29 PSCs.
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42 To overcome this bottleneck, 2D/3D hierarchical heterostructures have been
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44 proposed to combine the advantages of good charge transport of 3D perovskites and
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46 high stability of 2D perovskites.^[12-14] The formation of a 2D capping layer on the top
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48 surface of a 3D perovskite film can not only prevent moisture infiltration, but also
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50 work as a passivation layer to reduce the number of surface defects.^[15, 16] To date,
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52 Ruddlesden–Popper (RP) phase 2D perovskites are the most investigated systems for
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54 fabricating 2D/3D perovskite devices.^[15] The RP 2D perovskites have a general
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1 formula corresponding to $(A')_2(A)_{n-1}M_nX_{3n+1}$, where A is a small monovalent cation as
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4 in traditional 3D perovskites; A' is a larger monovalent spacer cation that forms a
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6 double organic layer intercalated into the inorganic sheets of perovskites; M is a
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8 divalent metal ion; X represents a halide anion; and n refers to the number of
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10 inorganic $[MX_6]^{4-}$ layers.^[17, 18] The organic spacer cations (also referred to as ligand
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12 molecules) designed and synthesized for RP-phase perovskites generally contain one
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14 terminal ammonium group that interacts with the anionic sheets in the octahedron
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16 frameworks, both Coulombically and through hydrogen bonds.^[8] The other part of the
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18 organic cations usually features alkyl segments that interact with the adjacent
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20 segments via van der Waals forces.^[6,7]
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28 To manipulate the interface properties and the related device performance of
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30 2D/3D PSCs, much progress has been made through the introduction of heteroatoms
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32 or the variation of the chain lengths of the organic spacers.^[19, 20] For example,
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34 Nazeeruddin et al. reported that the fluorinated spacer ligand,
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36 perfluorobenzylammonium, can induce a regular QW arrangement along the in-plane
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38 orientation and provide a much enhanced surface passivation effect of the 2D capping
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40 layer; the corresponding 2D/3D PSCs have an efficiency of 21.65% and retain 86% of
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42 the initial efficiency after continuous light illumination for 1100 h.^[19] Seok et al.
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44 found that improvements in electron-blocking and humidity-resistance ability can be
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46 achieved through increasing the alkyl-chain length of the spacer cations. For instance,
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48 octylammonium-based 2D/3D cells exhibit a stabilized efficiency of 22.9% with
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50 enhanced humidity stability as compared to 3D PSCs.^[20]
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1 In contrast to the widely studied RP-phase perovskites, diammonium-based 2D
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4 perovskites (with a general formula of $(A')(A)_{n-1}M_nX_{3n+1}$) feature organic dications as
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6 the spacer layers that bridge adjacent inorganic slabs.^[8] The resulting formation of
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8 strong hydrogen-bonding interactions at both ends of the spacer molecules orients the
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10 structure along the stacking direction.^[21] The diammonium spacers leave substantially
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12 lower degrees of freedom for interlayer displacements, which contributes to an
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14 increased stability of the crystal structure with respect to their RP-phase analogues.^{[18,}
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^{22]} It has been shown that diammonium-based ditopic ligands can facilitate the formation of a stable 2D phase with a homogeneous crystal structure and further improve the film stability, thus showing a great potential for application in 2D/3D PSCs.^[23]

To design the next generation of diammonium-based 2D perovskites for high-performance 2D/3D heterostructure PSCs, a systematic study of their structure-properties relationships is required. Also, an in-depth understanding of the ligand/spacer effects, including their molecular structure and spacer concentration, on the eventual QW structures within the multi-phase heterostructures, is needed. In addition, we note that, in the course of the formation of the 2D/3D structures, a rapid cation exchange can occur during the post-annealing process. Therefore, achieving high-quality 2D/3D heterostructures with controllable QW structures, optimized film textures, as well as good surface passivation properties and charge transport kinetics has proven to be challenging.^[15, 24]

Here, we seek to gain insight into the structure-properties relationships in

1 diammonium-based 2D/3D perovskite heterostructures. Three iodized diammonium
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3 ligands, consisting of 1,3-propanediammonium (PDA, $\text{H}_3\text{N}(\text{CH}_2)_3\text{NH}_3^{2+}$),
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6 1,6-diaminohexane ammonium (HDA, $\text{H}_3\text{N}(\text{CH}_2)_6\text{NH}_3^{2+}$) and
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9 2,2-(ethylenedioxy)bis(ethylammonium) (EDBE, $\text{H}_3\text{N}(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{NH}_3^{2+}$)
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11 were selected to study the effects of chain length and heteroatom incorporation on the
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13 related QW structures and interfacial properties of the 2D capping layer. The inclusion
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15 of oxygen atoms in the EDBE cations is expected to enhance their intermolecular
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17 interactions within the spacer layer and facilitate their coordination with the inorganic
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19 octahedral layers. Grazing incidence wide-angle X-ray scattering (GIWAXS) was
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21 used to examine the influence of the spacer structures and processing conditions on
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23 the formation of the capping layer and its orientation and uniformity in the 2D/3D
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25 perovskite. Density functional theory (DFT) calculations were performed to study the
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27 electronic structures and interfacial energy-level alignments of various 2D/3D
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29 perovskite films; the intermolecular interactions within the spacer layers were also
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31 evaluated. Interfacial charge transfer was probed via transient absorption spectroscopy.
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34 The impact of the QW arrangement, surface passivation, and band-energy alignment
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36 on charge transport and eventual photovoltaic performance was investigated as well.
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39 Overall, we show that a proper design of the spacer ligands makes it possible to
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42 fabricate 2D/3D PSCs with much improved power conversion efficiency and stability.
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Results and Discussion

Surface quantum well structure and orientation

A $\text{Cs}_{0.05}(\text{FA}_{0.85}\text{MA}_{0.15})_{0.95}\text{PbI}_3$ bulk perovskite film (taken as control case) was prepared from a precursor solution with 5 mol% excess PbI_2 based on a solution concentration of 1.5 M. A one-step anti-solvent dripping method was used to control the growth of the 3D perovskite film followed by a thermal annealing process. The 2D/3D hierarchical heterostructures were then fabricated by spin coating the isopropyl alcohol (IPA) solution containing the iodized organic ligands on the as-prepared 3D perovskite film, followed by a post thermal treatment process at 100 °C for 20 min (see **Figure 1**). The diammonium spacer cations were confined to the top surface due to their large molecular size and further reacted with PbI_2 to form a 2D capping layer on the 3D bulk film.

We started by exploring the influence of molecular structure and spacer concentration on the phase purity and orientation of the quantum wells (QWs) within the resultant 2D capping layer. The microstructures and crystallinities of the 2D/3D perovskite films, prepared by adding the spacers at various concentrations (from 2.5 to 5 and 10 mg mL⁻¹) were studied using grazing incidence wide-angle X-ray scattering (GIWAXS); the results are shown in **Figure 2a, 2b**, and **S1**. The GIWAXS pattern for the control film in the absence of ligand deposition exhibits scattering peaks at $q=1.0 \text{ \AA}^{-1}$ and $q=0.81 \text{ \AA}^{-1}$, which correspond to the photoactive perovskite α -phase and the non-perovskite hexagonal δ -phase, respectively (**Figure S2**).^[16] From the GIWAXS results, we observe that the EDDBE diammonium salts promote more

1 facile formation of the 2D perovskite layer with a well-defined n value, followed by
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4 HDA and then PDA.
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7 In the PDA case, the diffraction arc of the 2D perovskite phase can only be
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9 observed for a high concentration of the PDAI₂ solution. According to the line-cut
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11 profiles of the GIWAXS patterns along the in-plane orientation of the PDA-based
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13 2D/3D films prepared from different PDAI₂ concentrations (**Figure 2c**), the
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15 diffraction peak for the 2D structure, which locates at $q=0.44 \text{ \AA}^{-1}$, is only observed at
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17 a high PDAI₂ concentration of 10 mg/ml. The calculated d -spacing of 14.3 \AA is
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19 consistent with the lattice parameter of the PDA(FA)Pb₂I₇ ($n=2$) perovskite.^[25] The
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21 additional diffraction peak at $q=0.5 \text{ \AA}^{-1}$ is ascribed to the PDA-related intermediate
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23 complex.^[26, 27] The poor formation ability of the 2D structure can be attributed to their
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25 short propane backbone and thus a weaker degree of interactions among the PDA
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27 molecules, making it less favorable to form the 2D layer. In the case of the
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29 HDA-based perovskite films, the 2D layer structure is easier to form. At low ligand
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31 concentration, the HDA-based film exhibits a diffraction arc in the small-angle region
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33 at $q=0.65 \text{ \AA}^{-1}$ (d -spacing of 9.6 \AA), indicating the formation of intermediate
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35 perovskite complexes.^[28] When the HDAI₂ concentration increases to 5 mg/ml, a
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37 diffraction signal of the 2D phase appears at $q=0.56 \text{ \AA}^{-1}$ with a d -spacing of 11.3 \AA ,
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39 which corresponds to the 2D HDAPbI₄ ($n=1$) perovskite along both in-plane and
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41 out-of-plane orientations (**Figure 2d** and **S3**). In addition, the XRD pattern of the
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43 HDA-based 2D/3D film also shows a diffraction peak at $2\theta=7.8^\circ$, which further
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45 confirms the formation of a 2D layer structure on the surface (**Figure S4**). When the
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1 concentration further increases to 10 mg/ml, the HDA-based 2D/3D film exhibits an
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3 additional diffraction arc located at $q=0.35 \text{ \AA}^{-1}$, which corresponds to a d -spacing of
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5 17.8 \AA . Considering that the length of PbI_6^{4-} octahedra is determined to be ca. 6.3 \AA ,
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7 we deduce that the newly-formed phase is a 2D HDA(FA) Pb_2I_7 ($n=2$) perovskite
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9 oriented mainly along the out-of-plane direction (**Figure S3**).^[7] Therefore, the
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11 formation of an intermediate phase in the HDA-based perovskite films is seen to
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13 affect the crystallization process of the 2D capping layer and result in a broad phase
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15 distribution (coexistence of $n=1$ and $n=2$) and inhomogeneous crystal orientation of
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17 QWs on the 3D perovskite film.
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26 For the EDBE-based samples, distinct differences in crystallization behavior are
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28 indeed observed. Notably, a single-phase QW structure with corresponding diffraction
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30 peak at $q=0.43 \text{ \AA}^{-1}$, which is determined to be a 2D EDBEPbI₄ perovskite ($n=1$) with
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32 d -spacing of 14.7 \AA , is detected in all samples regardless of ligand concentration
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34 (**Figure 2e**).^[29] Such a lattice spacing is also in good agreement with the XRD study,
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36 showing a corresponding 2D perovskite diffraction signal 2θ at 6.0° (**Figure S4**). The
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38 strong coordination effect between the EDBE cations and the perovskite octahedral
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40 framework may lead to a reduced formation barrier for the 2D perovskites. This is
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42 confirmed by the X-ray photoelectron spectroscopy (XPS) measurements probing the
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44 chemical interactions between the EDBE cations and perovskite. As shown in **Figure**
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46 **S5**, both the control and EDBE-based 2D/3D films have O 1s peaks, but at different
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48 binding energies. The peak with the higher binding energy at 532.7 eV in the 3D
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50 perovskite film is attributed to adsorbed oxygen molecules from the air, while the
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1 peak at 531.1 eV in the EDBE-based case corresponds to an oxygen signal from a
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3 metal-oxygen bond.^[29, 30] This is further verified by the shift of the Pb 4f peaks to
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5 lower binding energies, which is consistent with the formation of a Pb-O coordination
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7 bond.^[31] The C 1s core-level energy spectra show clear molecular signature peaks
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9 (C-C, C-N, C-O) of the EDBE ligands. In the case of the 3D perovskite sample, the
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11 C=O peak (288.3 eV) associated with ambient contamination is detected, while such a
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13 signal in the EDBE-based film is significantly suppressed, which indicates that the 2D
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15 capping layer can provide good protection to the absorber layer from exposure to
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17 ambient environment.
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26 Based on the GIWAXS and XPS results, we suggest that the stronger
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28 coordination effect between EDBE cation and Pb^{2+} facilitates the direct phase
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30 transition into a 2D perovskite phase with formation of a phase-pure EDBEPbI_4
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32 component, which is consistent with the wider processing window of the EDBE-based
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34 2D/3D PSCs. When the ligand concentration further increases to over 2.5 mg/ml, the
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36 out-of-plane orientation of the QWs tends to strengthen (**Figure S3**). A higher
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38 concentration of iodized spacers leads to a deviation of the crystal packing from the
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40 parallel orientation and the coexistence of QWs with both in-plane and out-of-plane
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42 textures. The increased disorder of the QWs within the 2D capping layer is expected
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44 to augment the barrier for charge transport along the vertical direction and reduce the
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46 charge collection efficiency and corresponding device parameters. The detailed
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48 schematic models comprising the QW component and orientation for representative
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50 HDA- and EDBE-based 2D/3D films under various ligand concentrations are shown
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1 in **Figure 2f**. By examining the QW textures, it is clear that the choice of organic
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3 ligands in 2D/3D perovskites plays a critical role in the orientation and component
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5 control of the surface QWs.
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10 **Film morphology and energy-level alignment**

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12 To understand how the ligand structure can affect the morphology of the 2D/3D
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14 perovskite films, scanning electron microscopy (SEM) and atomic force microscopy
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16 (AFM) studies were conducted for films before and after the deposition of the iodized
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18 spacers. Here, we selected a ligand concentration of 5 mg/ml for consistent
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20 comparison among all samples. The cross-sectional scanning electron microscopy
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22 (SEM) images for the representative EDBE-based 2D/3D film and the control 3D film
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24 show well-connected perovskite crystal grains with good film quality in both cases.
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27 The thicknesses of the control 3D and 2D/3D films were determined to be ca. 780 nm
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29 and 800 nm, respectively (**Figure S6**). The plane-view SEM image of the control film
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31 reveals distinct white phases at the grain boundaries, which corresponds to residual
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33 PbI_2 on the perovskite surface (**Figure 3a**).^[32] With the introduction of PDAI_2 , the
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35 PbI_2 phases are almost eliminated. However, no distinct morphology change is
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37 detected in the PDA-based film, indicating there is no 2D perovskite phase formed,
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39 which is consistent with the GIWAXS patterns discussed above. By contrast, the SEM
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41 images of the HDA- and EDBE-based films show a distinctive lamellar morphology
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43 with less apparent grain boundaries compared to the control film, which illustrates the
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45 formation of a compact and uniform 2D capping layer on the 3D perovskite surface.
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1 In addition, the ligand-decorated films also show a reduction in root-mean-square
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3 (RMS) roughness, as indicated in the AFM images (**Figure S7**). The presence of the
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6 2D capping layer further decreases the roughness from 16.7 nm for the control film to
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9 below 7.0 nm for the HDA- and EDBE-based 2D/3D films. These observations
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12 suggest better surface quality of the hierarchical films.
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15 The effect of the different ligands on the energy-level alignment in the 2D/3D
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17 films was also investigated. In **Figure 3b**, the UV-vis absorption spectra of the control
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19 3D film and ligand-decorated films prepared from a ligand concentration of 5 mg/ml
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22 show that all the samples exhibit similar absorption spectra. The corresponding
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25 Tauc-plots all show the excitonic peak of the 3D phase at ca. 1.54 eV, which
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28 represents the optical gap of the films (**Figure S8**). The results indicate that the 2D
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31 capping layers show negligible influence on the light absorption property and energy
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34 gap of the perovskite films.^[16] To further determine the electronic structure of the
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37 control and 2D/3D films, an ultraviolet photoelectron spectroscopy (UPS) study was
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40 conducted (**Figure S9**). The valence band maximum (VBM) of the perovskite films
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43 were determined to be -5.65 eV, -5.64 eV, -5.60 eV, and -5.55 eV for the control,
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46 PDA-, HDA- and EDBE-based films, respectively. The conduction band minimum
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49 (CBM) was then roughly evaluated by subtracting the optical gap from the E_v , a
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52 procedure that neglects the impact of the excitonic effects; the corresponding energy
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55 levels for the perovskite films are shown in **Figure 3c**. Due to the absence of a 2D
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58 perovskite phase, the energy levels of the PDA-based film present a negligible shift
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61 with respect to the control film. By contrast, a better energetic alignment between the
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1 VBMs of the 2D/3D perovskites and the highest occupied molecular orbital (HOMO)
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4 level of the hole transport layer (HTL) is obtained, with the energetic difference
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6 reduced from 0.45 eV for the 3D case to 0.40 eV and 0.35 eV for the HDA- and
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8 EDDBE-based films, respectively. This better energy level alignment is expected to
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10 improve carrier extraction efficiency and the V_{oc} and FF parameters of the devices.^[33]
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15 To further understand the electronic structures and interface energy-level
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17 alignments of the 2D/3D perovskite films, we also performed density functional
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19 theory (DFT) calculations based on a repeated slab approach (see Methodology in the
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21 Experimental Section and the optimized lattice parameters in **Table S1**). Each
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23 **heterostructure** model consists of a slab of 3D FAPbI₃ (we note that the FA cation was
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25 considered in the 3D perovskite model since it represents the major component in the
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27 mixed-cation perovskite studied experimentally) and a layer of 2D $n=1$ perovskite
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29 with PDA, HDA, and EDDBE as the spacers. The density of states (DOS) of the 2D/3D
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31 **heterostructure** models were calculated at the HSE-SOC level and projected to the 2D
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33 and 3D components, respectively (**Figure 3d** and **3e**). Distinct characteristics in the
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35 band edge states can be observed in the projected DOS (PDOS), which lead to
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37 varying energy-level alignments at the 2D/3D interface. In the case of the HDA-based
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39 2D/3D system, the VBM and CBM of the **heterostructure** are dominated by
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41 contributions from the PbI₄²⁻ in the 2D layer and bulk FAPbI₃ phase, respectively,
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43 which results in the formation of a type-II junction (**Figure 3f**). Interestingly, the
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45 PDOS of the EDDBE-based system shows an enhanced DOS at the valence band edge,
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47 where the contributions are associated with both the 2D and 3D components. The
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1 charge density related to this state is distributed over the PbI_4^{2-} layers in both 2D and
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4 3D structures. By contrast, the VBM and CBM in the PDA-based heterostructures are
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6 dominated by the contributions of the bulk FAPbI_3 , with the 2D contributions
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8 appearing at energies slightly lower [higher] than the VBM [CBM]. The presence of
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10 such a type-I band alignment at the $\text{PDAPbI}_4/\text{FAPbI}_3$ heterostructure leads to a higher
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12 energy barrier for the charge transfer processes than in the other two cases.
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17 In addition to the energy-level alignments between the 2D and 3D components,
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19 we also calculated the VBM and CBM energetics with respect to the vacuum level in
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21 each system. As shown in **Figure 3f**, the VBMs of the HDA- and EDBE-based
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23 systems are 6.31 and 6.14 eV below the vacuum level, respectively, which
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25 corresponds to an upward VBM shift by 0.17 eV in the EDBE-based system vs. the
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27 HDA case. This is consistent with the VBM shift of ~ 0.05 eV observed in the UPS
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29 experiments for the HDA- and EDBE-based 2D/3D perovskite films (**Figure 3c**).
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31 Therefore, the calculations underline that the stronger interactions between the EDBE
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33 spacers and the perovskite layers can lead to an enhanced electronic density of states
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35 at the valence band edge and a reduction in the energy difference between the
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37 perovskite and HTL frontier levels. These results further highlight the important
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39 effects of ligand modifications on the overall device performance.
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51 While the 2D/3D heterostructure formation is a complex kinetic process that
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53 prevents us from a comprehensive first-principles investigation, we analyzed how
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55 strongly the organic spacers interact with one another within the spacer layer, in
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57 particular to understand how significantly the incorporation of oxygen atoms in
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EDBE affects the intermolecular binding energies. To do so, we considered dimers of neutral PDA, HDA, and EDBE molecules, in the absence of the perovskite layers and with the molecular geometries fixed at those optimized for the 2D/3D heterostructure models. The components of the intermolecular interaction energies were obtained via symmetry-adapted perturbation theory (SAPT) conducted at the SAPT0/6-31G(d,p) level; the results are given in **Table S2**. Our calculations show that the EDBE dimer has the largest total interaction energy, on the order of 10 kJ/mol; the interaction energy goes down by a factor of ~ 2 in the HDA dimer, and ~ 5 in the PDA dimer. In all three systems, the dispersion forces dominate the interactions; the EDBE dimer has also a large electrostatics component, which is however compensated by a significant exchange-repulsion term coming from intermolecular wavefunction overlap. We note that the vanishing exchange-repulsion term for the PDA dimer is due to the much larger intermolecular distance, ~ 4.2 Å on average, vs. ~ 2.8 Å and ~ 2.9 Å for the HDA and EDBE dimers, respectively.

Surface passivation and optoelectronic properties of the perovskite films

Having assessed the impact of ligand structure on the QW structure, film quality, and energetic alignments, we further seek to understand the effects of molecular passivation on the optoelectronic properties and charge dynamics of the 2D/3D heterostructures by a combination of electrical and optical spectroscopy studies. Space charge limited current (SCLC) measurements were conducted to quantify the trap densities in the studied perovskite films. We estimated the trap densities by

measuring the dark current–voltage curves of electron-only devices with a configuration of ITO/SnO₂/perovskite/PCBM/Ag, and hole-only devices with a configuration of ITO/PEDOT:PSS/perovskite/Spiro-OMeTAD/MoO₃/Ag (**Figure S10**). The trap density (n_{trap}) was calculated by the following equation:^[34]

$$n_{\text{trap}} = \frac{2\varepsilon_0\varepsilon_r V_{\text{TFL}}}{eL^2} \quad (1)$$

where ε_0 represents the vacuum permittivity, ε_r the relative dielectric constant, V_{TFL} the onset voltage of the trap-filled limit region, e the elementary charge, and L the thickness of absorber layer. In the case of the control film, the electron and hole trap densities are determined to be 6.3 ± 1.2 and $3.7 \pm 0.4 \times 10^{15} \text{ cm}^{-3}$, respectively (**Figure 4a**). Due to the incomplete phase transition of PDAI₂ into a 2D perovskite, the organic salt itself on the surface can act as trap site, which increases the electron and hole trap densities of the PDA-based films to 7.2 ± 1.0 and $4.7 \pm 1.1 \times 10^{15} \text{ cm}^{-3}$, respectively. By contrast, the electron trap densities reduce to 3.3 ± 1.1 and $2.2 \pm 0.7 \times 10^{15} \text{ cm}^{-3}$ and the hole trap densities reduce to 1.9 ± 0.5 and $1.7 \pm 0.5 \times 10^{15} \text{ cm}^{-3}$ for the HDA- and EDBE-based 2D/3D films, respectively, values that are significantly lower than those of the control film. These results indicate that the 2D capping layer can effectively suppress surface trap states. The lower trap densities obtained in the EDBE-based 2D/3D films with respect to the HDA-cases are attributed to the strong coordination effect between the EDBE cations and perovskite, as discussed in the XPS section. The suppression of trap states at the interface is beneficial as it reduces charge accumulation and improves charge collection efficiency.

To determine the influence of spacer modification on the recombination loss in

1 the 2D/3D perovskites, steady-state photoluminescence (PL) and time-resolved
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3 photoluminescence (TRPL) measurements were performed. **Figure 4b** illustrates a
4
5 significantly increased intensity of the emission peak in the HDA- and EDBE-based
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7 2D/3D perovskite films compared to the control 3D film (all films coated on glass
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9 substrates), which suggests a strong suppression of trap-induced emission quenching
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11 in the 2D/3D films. The enhanced radiative efficiency is expected to increase the
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13 degree of quasi-Fermi level splitting, which in turn leads to better V_{oc} .^[35] The
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15 relatively weak PL intensity of the PDA-based sample can be attributed to the
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17 accumulation of organic salts on the perovskite surface, which act as trap sites and
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19 induce a more severe nonradiative recombination loss. TRPL measurements were also
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21 performed to study the charge transport dynamics in the various samples and the
22
23 corresponding results are shown in **Figure 4c**. The decay curves were fitted with a
24
25 biexponential decay function as follow:^[16]
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$$I(t) = A_1 e^{-(t-t_0)/\tau_1} + A_2 e^{-(t-t_0)/\tau_2} \quad (2)$$

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29 where τ_1 and τ_2 are the fast and slow decay time constants, and A_1 and A_2 are the
30
31 corresponding decay amplitudes, respectively. The fitted parameters are summarized
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33 in **Table S3**. The control film exhibits an average lifetime (τ_{ave}) of 125.9 ns, which
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35 decreases to 23.9 ns for the PDA-based sample and increases to 217.4 and 271.1 ns
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37 for the HDA- and EDBE-based 2D/3D films, respectively. These results are consistent
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39 with the PL study, as they confirm that the efficient passivation effect provided by the
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41 2D capping layer prolongs the emission lifetime of the perovskite films.
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59 The charge dynamics in the 2D/3D **heterostructure** films were also studied by
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1 ultrafast transient absorption (TA) spectroscopy with a femtosecond laser pulse. The
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4 photo-induced variations in the absorption (ΔA) spectra were subsequently probed by
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6 a time-delayed laser-generated white light probe pulse. Due to the detection limit, it is
7
8 hard to capture the absorption signatures below 500 nm. However, the excitonic
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10 absorption peaks of $n=1$ 2D HDAPbI₄ and EDBEPbI₄ phases were both reported to
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12 appear at ca. 480 nm.^[29, 36] Based on the GIWAXS results, the HDA-based 2D/3D
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14 film prepared with a ligand concentration of 10 mg/ml comprises multi-phase QW
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16 components ($n=1, 2$), which was the reason for its selection for the TA study. **Figure**
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18 **S11** shows the TA spectra taken at various delay times for the HDA-based film under
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20 front-side excitation. The signal from the $n=2$ QW phase is observed at 578 nm,
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22 which is consistent with the observation of that phase component in the GIWAXS
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24 results. The dynamic evolution of the bleaching recovery in the HDA-based 2D/3D
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26 film was also extracted; it demonstrates that the appearance of the 3D bleaching
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28 signal is accompanied by a fast attenuation of the 2D bleaching signal. As for the
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30 similar phenomena reported in the RP-phase 2D/3D perovskite systems, these results
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32 indicate that photo-excited electrons can spontaneously transfer from lower n phases
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34 to the 3D phase, which is accompanied by the reverse flow of holes.^[37, 38] It is worth
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36 noting that this is the first report giving direct evidence of a spontaneous charge
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38 transfer process detected at diammonium-based 2D/3D heterostructures within a
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40 sub-ps time scale.
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56 After evaluating the trap density, recombination loss, and carrier dynamics of the
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58 perovskite films, electrical impedance spectroscopy (EIS) was performed to examine
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1 the associated transport and recombination resistances in perovskite devices. **Figure**
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4 **4d** shows the Nyquist plot of the PSCs measured at V_{oc} under dark condition. The
5
6 fitted equivalent circuit model is composed of the series resistance (R_s) and contact
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8 resistance (R_{co}), which are related to the high-frequency region in EIS plots, and the
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10 recombination resistance (R_{rec}), which is assigned to the low-frequency arc (**Figure**
11
12 **S12**).^[39] The fitting parameters calculated from the equivalent circuit model are listed
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14 in **Table S4**. The R_{co} and R_{rec} show distinctive changes among the four cases, which
15
16 represent the charge transport and recombination features at interfaces, respectively.
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18 The HDA- and EDBE-based 2D/3D cells exhibit lower R_{co} of 18.8 Ω and 15.0 Ω and
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20 higher R_{rec} of 6486 Ω and 9395 Ω compared to those values in control cell (27.5 Ω
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22 and 4196 Ω), which points to a much improved charge-carrier transfer and a
23
24 suppressed charge recombination in the 2D/3D **heterostructure**. However, in the
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26 PDA-based device, both R_s and R_{co} increase and R_{rec} decreases, which can be
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28 attributed to the increased surface trap density as well as the aggregation of insulating
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30 PDAI₂ salts on the contact interface.

31 **Photovoltaic performance and long-term stability**

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34 Finally, we evaluated the cell performances including the photovoltaic properties
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36 and stability. The photovoltaic devices were fabricated with an n-i-p architecture of
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38 indium tin oxide (ITO)/SnO₂/perovskite/Spiro-OMeTAD/MoO₃/Ag (**Figure 5a**). The
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40 *J-V* curves under AM 1.5G one-sun illumination and the corresponding photovoltaic
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42 parameters for the PSCs processed with different ligands and ligand concentrations
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are summarized in **Figure S13** and **Table S5**. The J - V curves of the champion device for each case are shown in **Figure 5b**. The control devices show a PCE_{max} of 20.1% (average PCE of $19.2 \pm 0.6\%$ for 50 cells), with a V_{oc} of 1.08 V, a J_{sc} of 23.8 mA cm^{-2} , and a fill factor (FF) of 78.2%. The PCEs of the PDA-based cells decrease with increasing ligand concentration due to the aggregation of the residual insulating PDAI_2 , which deteriorates the charge extraction contact. For the HDA- and EDBE-based 2D/3D heterostructure, the optimal devices are achieved at ligand concentrations of ~ 2.5 - 5.0 mg/mL . In general, under a relatively low concentration of organic ligands, the incomplete surface coverage and phase transition of the 2D capping layer limits the surface passivation effect at the 2D/3D heterostructure. On the contrary, too much of the ligand can result in the formation of a thick 2D capping layer, which can adversely affect the charge transport properties at the heterostructure interface and decrease the device efficiency. For the 2D/3D devices, higher PCE_{max} values of 21.7% (average PCE of $20.9 \pm 0.5\%$) for the HDA-based devices and 22.6% (average PCE of $21.6 \pm 0.4\%$) for the EDBE-based devices are obtained from a ligand concentration of 5.0 mg/mL and 2.5 mg/mL , respectively. This PCE value of 22.6% is among the highest reported for 2D/3D PSCs with diammonium spacers.^[29,40-43] Moreover, the photocurrent hysteresis behavior was also studied based on the following hysteresis index equation:^[44]

$$\text{Hysteresis index} = \frac{\text{PCE}_{\text{reverse}} - \text{PCE}_{\text{forward}}}{\text{PCE}_{\text{reverse}}} \quad (3)$$

The detailed device parameters are summarized in **Table S6** and both the forward and reverse scans of the J - V curves under illumination for the champion devices are

1 shown in **Figure S14**. The control device exhibits clear J - V hysteresis with a
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4 hysteresis index of 7.8%, whereas those of the HDA- and EDBE-based 2D/3D
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6 devices decrease to 3.7% and 2.4%, respectively. We attribute the reduced hysteresis
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8 of the devices to the enhanced surface trap passivation effect of the 2D/3D films. The
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10 statistics of the photovoltaic parameters for 50 devices are also shown in **Figure S15**,
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12 further confirming the efficiency enhancement and the superior reproducibility for the
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14 2D/3D devices compared to the control ones. The key photovoltaic parameters that
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16 contribute to the efficiency improvement of the 2D/3D PSCs are J_{sc} and V_{oc} . The
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18 corresponding external quantum efficiency (EQE) spectra of champion cells for the
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20 different cases are illustrated in **Figure 5c**. The integrated values of the current
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22 density for the control, PDA-, HDA-, and EDBE-based devices were determined to be
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24 23.5, 22.5, 24.1, and 24.7 mA cm⁻², respectively, which are in good agreement with
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26 the J_{sc} values obtained from the corresponding J - V curves. In order to further assess
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28 the device characteristics, we tested the stabilized power output under standard
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30 one-sun illumination at a fixed maximum power point (MPP) voltage (**Figure 5d**).
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32 The HDA- and EDBE-based 2D/3D devices exhibit better photostability under
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34 illumination, with the PCEs stabilized at 21.5% and 22.3%, respectively, whereas the
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36 PDA case shows a slight PCE drop with time and stabilizes at 14.8%. These results
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38 indicate that the reduced surface trap in 2D/3D heterostructure is conducive to a stable
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40 power output under long-term operational condition. To evaluate the compatibility of
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42 this spacer post-treatment strategy for larger area devices, we also fabricated the
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44 2D/3D solar cells with an active area of 1.0 cm². Benefiting from the good interfacial

1 properties of the 2D/3D heterostructure, a good PCE of 20.3%, with a FF of 77.9%, a
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4 V_{oc} of 1.09 V, and a J_{sc} of 24.1 mA cm⁻², was achieved for the best-performing EDDBE
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6 based device, which is better than the PCE of 17.4% for the best control device
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9 (Figure S16 and Table S7).”

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12 We now further investigate the device physics to gain better insight into the
13 effects of ligand structure on charge collection efficiency and trap-assisted
14 recombination in the devices. As illustrated in Figure S17, the light
15 intensity-dependent V_{oc} curves were fitted to obtain the $\eta k_B T/q$ slope, where η
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17 represents the ideality factor, k_B is the Boltzmann constant, T is temperature and q is
18 the elementary charge.^[45,46] The fitted slopes are determined to be $1.40k_B T/q$ and
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20 $1.34k_B T/q$ for the HDA- and EDDBE-based 2D/3D devices, respectively, which are
21 smaller than those of the control ($1.52k_B T/q$) and PDA-based ($1.69k_B T/q$) devices.
22
23 Generally, the deviation in slope from $k_B T/q$ to $2k_B T/q$ suggests more severe
24 trap-assisted Shockley-Read-Hall recombination in devices.^[31] The reduced linear
25 slopes in 2D/3D devices indicate that the trap-assisted recombination loss is
26 remarkably reduced via the deposition of the 2D capping layer. The relationship
27 between the V_{oc} improvement and built-in potential (V_{bi}) within the different devices
28 was further evaluated by performing the capacitance-voltage ($C-V$) measurements. As
29 shown in Figure 5e, the V_{bi} values extracted from the intercept $1/C^2 = 0$ were
30 determined to be 0.94, 0.85, 0.99, and 1.0 V for the control, PDA-, HDA- and
31 EDDBE-based devices, respectively. The higher V_{bi} displayed by the 2D/3D devices
32 indicates that the built-in band alignment at the heterostructure contributes to a
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1 stronger driving force for charge separation, which in addition to the improved trap
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4 passivation effect, makes the photo-generated carrier collection at the perovskite/HTL
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6 interface more efficient. Also, a lower carrier density is detected at the 2D/3D
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8 **heterostructure** interface and is inversely proportional to the extracted slope values
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10 from the linear regime, which points to the fast charge transfer at the contact
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12 interface.^[47] In contrast, the control and PDA-based devices exhibit lower built-in
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14 potentials and higher residual charges at the contact interface, which is consistent with
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16 J_{sc} and V_{oc} trends obtained from the J - V curves.
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23 The charge recombination and extraction rates in the PSCs were studied using
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25 transient photocurrent (TPC) and transient photovoltage (TPV) measurements, the
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27 results are shown in **Figure 5f** and **S18**, respectively.^[48] It is apparent that the
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29 introduction of 2D/3D **heterostructure** reduces the charge extraction time and extends
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31 the charge recombination lifetime when compared to the control device. Among the
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33 ligand-modified devices, the EDBE-based 2D/3D devices present the best charge
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35 extraction efficiency and lowest recombination rate, which is fully consistent with the
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37 electrical and optical analyses we discussed above. That the best device performance
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39 is achieved in the EDBE-based 2D/3D PSCs among all studied solar cells, highlights
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41 the importance of ligand tailoring in 2D/3D hierarchical **heterostructures** for
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43 high-efficiency PSCs.
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53 The stability of the PSCs under various test conditions was then studied, which
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55 demonstrates significant improvement in device stability in the diammonium-based
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57 2D/3D perovskite cells. As one of the advantages of introducing hydrophobic organic
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1 ligands is to enhance the water resistance of the perovskite films, contact-angle
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4 measurements were carried out. As can be seen in **Figure 6a** and **S19**, the contact
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6 angles of water on the 2D/3D films increased by 40-50° with respect to the value of
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8 39.3° for the control film. The more regular QW orientation and pure $n=1$ component
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10 within the 2D perovskite layer contribute to the slightly higher contact angle of the
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12 EDDBE-based 2D/3D film. The hydrophobic 2D capping layer is expected to
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14 effectively prevent the penetration of moisture and retard the undesired phase
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16 transition of the FA-based perovskite from the α -phase to the inactive δ -phase. In
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18 contrast, the water contact angle of the PDA-based film reduces to 28.9°, even lower
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20 than the value of the control film. The exposed amine groups in the under-coordinated
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22 spacer dication on the surface tend to hydrogen bond with H₂O molecules and
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24 therefore lead to a more hydrophilic surface. Humidity stability tests were conducted
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26 by placing the unencapsulated devices in a chamber at 40% relative humidity at room
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28 temperature (**Figure 6b**). Based on the normalized PCE values measured as a function
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30 of storage time, the HDA- and EDDBE-based 2D/3D devices maintain 74% and 79% of
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32 their initial efficiency, respectively, after 40 days of exposure to ambient environment.
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34 These devices significantly outperform the control (51%) and PDA-based (37%)
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36 devices under the same aging conditions. We also observe that the unencapsulated
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38 2D/3D devices stored under a N₂-filled atmosphere at room temperature in the dark
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40 maintain their initial PCE well after 40 days (**Figure S20**). Importantly, in addition to
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42 the improved moisture resistance, the thermal stability of the 2D/3D perovskite cells
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44 is also enhanced. **Figure 6c** presents results from the thermal stability tests of the
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1 unencapsulated devices under constant heating at a temperature of 85 °C in a N₂-filled
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3 atmosphere. A more thermally stable poly[bis(4-phenyl) (2,4,6-trimethylphenyl)amine]
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5 (PTAA) was selected as the HTL for the thermal stability tests to avoid the negative
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7 influence of thermally activated ion diffusion from the *p*-dopants in
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9 Spiro-OMeTAD.^[31] The control and PDA-based cells exhibit rapid degradation within
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11 the first 150 h with their performance decreasing to 40% and 33% after 500 h
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13 continuous heating. The presence of 2D perovskite layers on the surface retard the
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15 thermal degradation of the corresponding 2D/3D PSCs, which maintain over 60% of
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17 the initial performance after same aging period. Moreover, the light stability was also
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19 monitored under AM 1.5G one sun continuous illumination for devices without
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21 encapsulation (**Figure 6d**). The 2D/3D cells also outperform the control device under
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23 continuous illumination, for the EDDBE-based device, the efficiency drops by less than
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25 15% after 500 h of illumination. Our results highlight that when a rationally designed
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27 ligand is employed to fabricate well-defined 2D/3D hierarchical perovskite structures,
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29 it is possible simultaneously to reduce the surface traps and charge recombination,
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31 improve the charge collection properties, enhance the water resistance, and increase
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33 the light and thermal stability of the devices. These collective effects not only result in
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35 PSCs with enhanced photovoltaic property, but also significantly improved
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37 environmental and operational stability, underlining the potential of using the 2D/3D
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39 heterostructure strategy to improve the overall performance of PSCs.
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Conclusion

In conclusion, we have provided new insights into the effect of ligand design on the structure-property-performance relationships in diammonium-based 2D/3D PSCs through a systematic study of the structural, optical, electronic, and electrical properties of 2D/3D perovskite heterostructures. The inclusion of heteroatoms into the molecular ligands is important to enhance their intermolecular interactions and facilitate their coordination with the $[\text{PbI}_6]^{4-}$ octahedral framework, thus effectively regulating the QW packing, orientation, and phase purity of the 2D capping layers; also, it provides a much-improved surface trap passivation effect for the 2D/3D heterostructure. As a result, in the optimized EDBE-based 2D/3D perovskite heterostructures, a phase-pure 2D perovskite capping layer ($n=1$) with a homogeneous orientation arrangement was demonstrated. A combination of UPS, DFT and Mott-Schottky analyses points to an energy level alignment that favors spontaneous charge transfer at the 2D/3D heterostructure. Overall, the improved 2D layer structure, surface passivation effect, and well-matched band alignment lead to EDBE-based devices with efficient charge transport kinetics at the 2D/3D interface and remarkably reduced nonradiative recombination loss. Thus, significant improvements in V_{oc} and J_{sc} values are achieved in the 2D/3D PSCs, with the EDBE-based PSCs delivering a champion PCE of 22.6%, which outperforms the 3D analogue (20.1%). The superior long-term stability of the 2D/3D devices under different aging scenarios demonstrates the robustness of the 2D phase against

1 environmental stimuli. We believe our work provides important insights into the
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3 impact of the ligand/spacer structure on the interfacial properties of the multi-phase
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5 perovskite **heterostructures** and offers a promising direction to further improve the
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7 performance and stability of PSCs.
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10 11 12 **Experimental section**

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15 *Materials:* All chemicals and solvents were used as received without further
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17 purification. SnO₂ colloid precursor (tin (iv) oxide, 15% in H₂O colloidal dispersion)
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19 was purchased from Alfa Aesar. Lead iodide (PbI₂, 99.9985%) was purchased from
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21 Tokyo Chemical Industry (TCI). Formamidinium iodide (FAI, ≥99.95%),
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23 methylammonium iodide (MAI, 99.5%), lead chloride (PbCl₂, 99.99%),
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25 1,3-propanediammonium iodide (PDA)I₂, 1,6-diaminohexaneammonium iodide
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27 (HDA)I₂, 2,2-(ethylenedioxy)bis(ethylammonium) iodide (EDBE)I₂,
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29 4-tert-butylpyridine (tBP, 96%), 2,2',7,7'-tetrakis
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31 (N,N'-di-p-methoxyphenylamine)-9,9'-spirobifluorene (Spiro-OMeTAD, ≥99.5%)
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33 and poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA, Mn=15000-25000)
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35 were purchased from Xi'an Polymer Light Technology Corp (p-OLED). Cesium
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37 iodide (CsI, 99.9%), N,N-dimethylformamide (DMF, 99.8%), dimethylsulfoxide
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39 (DMSO, 99.9%), and chlorobenzene (anhydrous, 99.8%) were purchased from
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41 Sigma-Aldrich.
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46 *Solution preparation:* The solution preparation was conducted under inert atmosphere
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48 inside a nitrogen glove box. The Cs_{0.05}(FA_{0.85}MA_{0.15})_{0.95}PbI₃ perovskite precursor
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1 solution was prepared by dissolving 0.075 M CsI, 1.21 M FAI, 0.21 M MAI, 1.575 M
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4 PbI₂, 0.05M PbCl₂ in 1 mL DMF and DMSO mixture solvent (4:1 v/v), and stirred
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6 overnight. The perovskite solutions were filtered prior to solution-casting. The iodized
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8 spacers (PDA)₂, (HDA)₂ and (EDBE)₂ were dissolved in isopropyl alcohol (IPA,
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10 99.9%, Aladdin) in different concentrations and heated at 70 °C for 5 min before
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12 solution-casting. The Spiro-OMeTAD solution was prepared by dissolving 90 mg
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14 Spiro-OMeTAD, 22 μL lithium bis(trifluoromethanesulfonyl) imide in acetonitrile
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16 and 36 μL 4-tert-butylpyridine in 1 mL chlorobenzene. For the PTAA solution used in
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18 device thermal stability test, PTAA doped with
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20 poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (TPFB) was dissolved in CB with a
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22 concentration of 30 mg/ml. and the weight ratio of PTAA/TPFB was 30:1. SnO₂
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24 colloid particles were diluted with deionized H₂O in the ratio of 1:6.5 before use.
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34 *Device fabrication:* The ITO-coated glass (1.5 cm × 1.5 cm) was cleaned by
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36 sequential sonication in deionized water, detergent, and isopropanol and then dried in
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38 an oven for 30 min each and then dried under N₂ flow and treated by ozone plasma
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40 for 5 min. The SnO₂ nanoparticle was spin-coated onto the cleaned ITO substrates at
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42 3,000 rpm for 30 s, followed by thermal annealing in air at 150 °C for 20 min. After
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44 depositing the electron transport layer, the perovskite layer was deposited under inert
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46 atmosphere inside a nitrogen glove box. The consecutive two-step spin-casting
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48 procedure was performed by 1000 rpm for 10 s followed with 4000 rpm for 40 s. At
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50 ca. 15 s before the end of the spin-coating step, 80 μl of CB was dropped onto the
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52 substrate. The substrates were then put onto a hotplate for 30 min at 100 °C. For
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1 ligand treatment, 45 μL of ionized spacer solution was dropped on the annealed
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3
4 perovskite film during a spin-coating procedure at 4000 rpm for 30 s, followed by
5
6 thermal annealing at 100 $^{\circ}\text{C}$ for 20 min. Subsequently, the hole transporting layers
7
8
9 were deposited on the top of the perovskite film by spin coating the Spiro-OMeTAD
10
11 solution at 5000 rpm for 30 s, the procedure for the PTAA solution was 4000 rpm for
12
13 30 s. Finally, a 12-nm MoO_3 layer and 100-nm silver (Ag) layer were thermally
14
15 evaporated under vacuum. A non-refractive mask was employed to determine the
16
17 active device area of 0.04 cm^2 .
18
19
20
21

22 **Characterization**

23
24
25
26 *Optical metrology:* UV-Visible absorption spectra were acquired on a PerkinElmer
27
28 UV-Lambda 950 instrument. Steady-state photoluminescence (PL) and time-resolved
29
30 photoluminescence (TRPL) were measured with Edinburgh Instruments Ltd
31
32 (FLS980).
33
34
35

36
37 *Electron microscopy:* The surface morphology and structure of the perovskite films
38
39 were characterized by SEM (FE-SEM; SU-8020, Hitachi) and Atomic Force
40
41 Microscopy (AFM, Park XE-100), respectively.
42
43
44

45
46 *X-ray diffraction (XRD)* measurements were carried out in a θ -2 θ configuration with a
47
48 scanning interval of 2 θ between 5 $^{\circ}$ and 60 $^{\circ}$ on a Rigaku Smart Lab (X-ray Source: Cu
49
50 $\text{K}\alpha$; $\lambda = 1.54 \text{ \AA}$).
51
52

53
54 *Grazing incidence wide angle X-ray scattering (GIWAXS)* measurements were
55
56 collected using a Xeuss 2.0 spectrometer (Xenocs company) with MetalJet-D2
57
58
59
60

1 (Excillum) as the X-ray source and Pilatus 3R 1M (Dectris) as the detector and were
2
3
4 performed on a ITO/SnO₂/perovskite structure.
5

6 *UPS measurements:* The valence band (VB) spectra were measured with a
7
8
9 monochromatic He I light source (21.22 eV) and a VG Scienta R4000 analyzer. A
10
11
12 sample bias of -5 V was applied to observe the secondary electron cutoff (SEC).
13

14 *X-Ray Photoelectron Spectroscopy (XPS)* results were acquired on a photoelectron
15
16
17 spectrometer (ESCALAB 250Xi, Thermo Fisher Scientific).
18
19

20 *Femtosecond pump-probe transient absorption (TA)* measurements: The femtosecond
21
22
23 laser pulse was generated by a Ti:sapphire femtosecond regenerative amplifier with
24
25
26 800 nm wavelength and 1 kHz repetition rate and served as both pump and probe
27
28
29 beams. The pump pulse with a wavelength of 450 nm and duration of 50 fs generated
30
31
32 via a second harmonic generator (SHG) was used to excite all the samples and the
33
34
35 probe beam was detected by a high-speed spectrometer (HELIOS, Ultrafast Systems).
36
37
38 The wavelength range of the detector was set from 500 to 900 nm, and the spot size of
39
40
41 TA was approximately 0.5 mm² as evaluated by imaging the laser spot. All
42
43
44 experiments were carried out at room temperature (i.e. $T=300$ K).
45

46 *Solar-cell characterizations:* The *J-V* performance of the devices were analyzed by
47
48
49 Keithley 2400 source under the nitrogen condition in the glovebox, and the
50
51
52 illumination intensity was 100 mW cm⁻² (AM 1.5G Oriel solar simulator). The scan
53
54
55 rate was 0.3 V s⁻¹. The delay time was 10 ms and the scan step was 0.02 V. The power
56
57
58 output of the lamp was calibrated by a NREL-traceable KG5 filtered silicon reference
59
60
61 cell. The device area of 0.04 cm² was defined by a metal aperture to avoid light
62
63
64
65

1 scattering from the metal electrode into the device during the measurement. The EQE
2
3
4 was characterized by the QTest Station 2000ADI system (Crowntech. Inc., USA), the
5
6 light source was a 300 W xenon lamp. The monochromatic light intensity for EQE
7
8
9 was calibrated with a reference silicon photodiode. Mott-Schottky analyses were
10
11
12 conducted using a multi-channel potentiometer (VMP3, Biologic) at the frequency of
13
14
15 50 KHz in the applied voltage range from 0 to 1.5 V with an AC amplitude of 25 mV.

16
17 *Trap-density measurements:* Electron-only devices (ITO/SnO₂/perovskite/PCBM/Ag)
18
19 and hole-only devices (ITO/PEDOT:PSS/perovskite/Spiro-OMeTAD/MoO₃/Ag) were
20
21
22 fabricated to evaluate the electron and hole mobilities in the devices. The dark *J-V*
23
24
25 characteristics of the electron (or hole)-only devices were measured by a Keithley
26
27
28 2400 source. The trap state density was determined by the trap-filled limit voltage
29
30
31 using equation 1.

32
33
34 *Transient photovoltage (TPV)* and *transient photocurrent (TPC)* measurements were
35
36
37 carried out with a Paios 4.0 instrument (FLUXiM AG, Switzerland).

38
39 *Electrical impedance spectroscopy (EIS)* measurements were conducted by using the
40
41
42 electrochemical workstation (IM6ex, Zahner, Germany) in the frequency range from
43
44
45 10 Hz to 4 MHz at open-circuit voltage in dark conditions.

46
47
48 *Contact angle measurements* were conducted on Dataphysics OCA-20 with a drop of
49
50
51 ultrapure water (0.05 mL). The photographs were taken 1 second after water dripping.

52
53 *Density functional theory (DFT) calculations* were carried out using the Vienna Ab
54
55
56 initio Simulation Package (VASP).^[49] Each slab unit cell of the 2D/3D heterostructure
57
58
59 consists of a $\sqrt{2} \times \sqrt{2} \times 3$ cubic FAPbI₃, a layer of the 2D n=1 perovskite containing

1 two A' organic spacer molecules (A' = PDA, HDA, and EDBE) and two PbI₆ units,
2
3 and a vacuum space of 15 Å. To minimize the lattice mismatch between the 2D and
4
5
6 3D crystal structures, the a and b lattice parameters of the 2D/3D heterostructure
7
8
9 models were fixed at the average a and b values of each fully relaxed 2D and 3D
10
11
12 crystals (**Table S1**), while the atomic coordinates of the heterostructure were fully
13
14
15 relaxed until the total force on each atom was less than 0.01 eV/Å. The geometry
16
17
18 optimizations were performed at the Perdew-Burke-Ernzerhof (PBE) level with
19
20 Spin-Orbit Coupling (SOC) and D3 van der Waals (VdW) corrections.^[50, 51] The total
21
22
23 and projected density of states were then calculated for each system using the
24
25
26 range-separated hybrid functional of Heyd-Scuseria-Ernzerhof including the SOC
27
28
29 corrections (HSE+SOC).^[52] The dipole-correction scheme as implemented in VASP
30
31
32 was applied to eliminate any spurious dipole-dipole interactions between the periodic
33
34
35 slabs. A plane-wave energy cut-off of 500 eV and a Γ -centered Monkhorst-Pack
36
37
38 k-mesh of $2 \times 2 \times 1$ were applied in all calculations.

39 *Energy-component analyses* for interaction energies in neutral PDA, HDA, and EDBE
40
41
42 dimers were performed using the PSI-4 package at the SAPT0/6-31G(d,p) level of
43
44
45 theory.^[53]
46
47
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50

51 **Supporting Information**

52
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54 Supporting Information is available from the Wiley Online Library or from the
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57 author.
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Conflicts of interest

The authors declare no conflicts of interest.

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